DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the manganese dry battery which used the negative electrode of the zinc alloy.
[0002]
[Description of the Prior Art]The structure of a manganese dry battery is shown in drawing 1. in drawing 1 -- 1 -- zinc (negative electrode) and 2 -- a separator and 3 -- as for a positive pole terminal board and 7, a carbon rod and 5 are [an insulating tube and 9] armor cans a negative pole terminal board and 8 an obturation object and 6 positive electrode mixture and 4. The zinc can (henceforth a negative electrode can) which serves as a container for many years has been used for the negative electrode of a manganese cell. By the way, the zinc alloy which contained 200-600 ppm cadmium and more lead than 50 ppm the giving ductility and a mechanical strength required in the case of that working for can manufacturing, and making corrosion resistance hold to the electrolysis solution which is contents of a negative electrode can purpose has been used for this zinc can.
[0003]However, it mixes in industrial waste or a domestic waste, and they have posed a problem as a causative agent of environmental pollution as they are harmful to a human body and their amount of consumption of that increases, although cadmium and lead which are contained in this zinc alloy are little. Although the prevention serves as pressing need now, use of the zinc alloy which contains neither cadmium nor lead in the negative electrode can of a manganese dry battery as the measure is desired strongly.
[0004]
[Problem(s) to be Solved by the Invention]However, the zinc alloy prepared from the zinc alloy currently used from the former only removing cadmium has a quite low mechanical strength as compared with a cadmium content zinc alloy, and a crack and modification arise in a dry cell

manufacturing process, and it causes an internal short circuit. The zinc alloy prepared from the zinc alloy only removing lead becomes easy to receive corrosion with the electrolysis solution in a cell as compared with a lead content alloy, and long-term-storage nature falls substantially.

[0005]This invention coped with the above-mentioned situation, was made, and does not contain cadmium and lead in a zinc alloy in the manganese dry battery using the negative electrode of the zinc alloy, but it aims at providing the manganese dry battery which moreover has a mechanical strength and corrosion resistance equivalent to the conventional negative electrode can.

[0006]

[Means for Solving the Problem]In order to attain said purpose, a zinc alloy which uses a manganese dry battery of this invention as a negative electrode contains one sort of 30-8000 ppm bismuth and 10-1000 ppm alkaline-earth metals (Mg, Ca, Sr, Ba), or two sorts or more to zinc weight.

[0007]

[Function]The bismuth contained as an ingredient of a zinc alloy in this invention makes corrosion resistance give a zinc alloy. The corrosion resistance with which the quantity of bismuth should be [the effect] a little satisfied of a certain thing by ingredient combination below 30 ppm is not acquired. If bismuth exceeds 8000 ppm, the effect which controls corrosion is not preferred in order not to acquire a prominent effect to the content of a certain thing but to increase a manufacturing cost rather. Still, the mechanism of action of the improvement of corrosion resistance to the electrolysis solution of the zinc alloy by addition of this bismuth is not clear.

[0008]While alkaline-earth metals (Mg, Ca, Sr, Ba) give a mechanical strength to a zinc alloy in this invention, strip-processing nature worsening by blending bismuth is made to improve. The quantity of these alkaline-earth metals cannot fully improve strip-processing nature in less than 10 ppm, but in exceeding 1000 ppm, the corrosion resistance of a zinc alloy becomes insufficient. One sort or two sorts or more may be sufficient as combination of alkaline-earth metals, and it is effective unless it deviates from the above-mentioned component amount.

[0009]Although impurities, such as copper of a ppm unit, iron, cadmium, and lead, mix in zinc unescapable in process of the scouring, in this invention, existence of inevitable impurities of this level does not become a problem.

[0010]

[Example]The example of this invention is described below. Using the zinc metal of 99.99 % of the weight or more of purity which carried out electrolytic scouring, bismuth, magnesium, calcium, strontium, and barium were blended with this, as shown in Table 1 and 2, respectively, the alloy sample was prepared, and it was considered as Examples 1-96.

Although elegance is made into the comparative example 1 (refer to Table 3) conventionally containing lead and cadmium, lead and cadmium are not contained but bismuth and alkaline-earth metals are contained for comparison, The quantity of bismuth and alkaline-earth metals prepared the zinc alloy which deviates from the range of this invention as the comparative examples 2-27 (refer to Table 4).

[0011]The following test evaluation was performed about these alloys. Here, n is the sample number in each example.

1) Corrosion weight loss (n= 3)

The mixture of phosphorus flaky graphite and way acid was used as lubricant for the zinc alloy pellet obtained by the examination of 3 strip-processing nature which carries out a postscript, and the negative electrode can was produced by the impact extrusion method. The negative electrode can was cleared, a 50x50-mm test piece was produced, the surface was ground until it became smooth with the sandpaper of #400 - 1200, and it was immersed in the electrolysis solution for manganese dry batteries which carried out weighing and was beforehand prepared after alkaline degreasing, rinsing, and desiccation, and stored within 45 ** constant temperature for 100 hours. The after-storage test piece was taken out, and weighing was rinsed, dried and carried out. The decrease of weight of the test piece was searched for, the value was **(ed) with the surface area of the test piece, and it was considered as corrosion weight loss (mg/cm^2).

[0012]2) The gas yield from a cell (n= 5)

Manganese dioxide 60 weight section of not less than 70% of purity, acetylene black 10 weight section, and zinc oxide 0.6 weight section are mixed well, Electrolysis solution 49 weight section of 25% of zinc-chloride-concentration weight and 2.0 % of the weight of ammonium chloride concentration could be added to this, it mixed, uniform positive electrode mixture was prepared, and this was made into the anode. On the other hand, the separator prepared for the negative electrode what applied the starch for electrolysis solution maintenance to kraft using the negative electrode can obtained by the corrosion-weight-loss examination of the above 1. R20 type dry cell was produced using such materials. Production cells were put in in the measuring cylinder which filled the liquid paraffin, it stored in 60 **, and upward displacement of the gas emitted was carried out into the cylinder. The storage time was carried out 20 days and read the gas volume which carried out upward displacement.

[0013]3) The strip-processing nature sample alloy (thickness 20mm width 100mm 500 mm in length) was rolled with the heating roller press with a temperature of 180-220 ** so that it might become a 5-mm-thick board. The number of the pellet obtained by piercing a sample alloy plate after rolling on R20 type hexagon-head pellet whose vertical angle is 31.0 mm was counted, the number of the pellet obtained from the owner lead alloy which performed the same operation was made into 100%, and the comparative figure with that was made into

strip-processing nature (%).

[0014]The number of the sample alloy with bad strip-processing nature of the normal pellet obtained by a crack and a crack occurring the surface and near both ends an alloy plate at the time of rolling, and a crack and a chip arising on the pierced pellet decreases.

[0015]

[Table 1]

No.	合金組成 (ppm)					腐食減量 (mg/cm²)	ガス発生量 (ml)	圧延加工性 (%)
	Bi	Mg	Ca	Sr	Ba			
1	30	10	0	0	0	4.56	170	90
2	30	0	10	0	0	4.56	171	90
3	30	0	0	10	0	4.57	170	91
4	30	0	0	0	10	4.58	172	91
5	30	100	0	0	0	4.54	168	92
6	30	0	100	0	0	4.56	171	93
7	30	0	0	100	0	4.57	171	93
8	30	0	0	0	100	4.55	170	92
9	30	500	0	0	0	4.55	169	94
10	30	0	500	0	0	4.55	170	94
11	30	0	0	500	0	4.57	172	94
12	30	0	0	0	500	4.56	172	95
13	30	1000	0	0	0	4.56	171	100
14	30	0	1000	0	0	4.57	171	100
15	30	0	0	1000	0	4.60	174	100
16	30	0	0	0	1000	4.59	173	100
17	100	10	0	0	0	3.95	157	94
18	100	0	10	0	0	3.98	158	95
19	100	0	0	10	0	4.00	160	95
20	100	0	0	0	10	3.97	157	94
21	500	100	0	0	0	3.25	150	94
22	500	0	100	0	0	3.28	153	95
23	500	0	0	100	0	3.29	155	96
24	500	0	0	0	100	3.26	150	95
25	1000	10	0	0	0	3.05	137	93
26	1000	0	10	0	0	3.08	140	94
27	1000	0	0	10	0	3.09	142	93
28	1000	0	0	0	10	3.06	138	94
29	1000	100	0	0	0	3.07	140	95
30	1000	0	100	0	0	3.09	141	96
31	1000	0	0	100	0	3.10	143	96
32	1000	0	0	0	100	3.08	140	95
33	1000	1000	0	0	0	3.06	138	100
34	1000	0	1000	0	0	3.10	142	100
35	1000	0	0	1000	0	3.11	142	100
36	1000	0	0	0	1000	3.09	141	100
37	2000	100	0	0	0	2.99	134	96
38	2000	0	100	0	0	3.01	135	96
39	2000	0	0	100	0	3.00	134	96
40	2000	0	0	0	100	3.02	136	96
41	5000	1000	0	0	0	2.97	133	100
42	5000	0	1000	0	0	2.98	134	100
43	5000	0	0	1000	0	2.99	135	100
44	5000	0	0	0	1000	2.98	134	100
45	8000	10	0	0	0	2.76	121	95
46	8000	0	10	0	0	2.76	122	96
47	8000	0	0	10	0	2.78	123	95
48	8000	0	0	0	10	2.77	122	96

[0016]

[Table 2]

No.	合金組成 (ppm)					腐食減量 (mg/cm²)	ガス発生量 (ml)	圧延加工性 (%)
	Bi	Mg	Ca	Sr	Ba			
49	8000	100	0	0	0	2.76	121	96
50	8000	0	100	0	0	2.75	120	97
51	8000	0	0	100	0	2.77	122	97
52	8000	0	0	0	100	2.79	123	96
53	8000	500	0	0	0	2.75	120	98
54	8000	0	500	0	0	2.78	122	99
55	8000	0	0	500	0	2.79	123	98
56	8000	0	0	0	500	2.77	123	99
57	8000	1000	0	0	0	2.76	121	100
58	8000	0	1000	0	0	2.77	122	100
59	8000	0	0	1000	0	2.78	122	100
60	8000	0	0	0	1000	2.76	121	100
61	30	10	10	0	0	4.55	170	95
62	30	500	500	0	0	4.57	172	100
63	30	10	0	10	0	4.56	171	95
64	30	500	0	500	0	4.57	172	100
65	30	10	0	0	10	4.56	171	96
66	30	500	0	0	500	4.57	171	100
67	30	0	10	10	0	4.58	172	96
68	30	0	500	500	0	4.59	173	100
69	30	0	10	0	10	4.56	171	96
70	30	0	500	0	500	4.58	172	100
71	30	0	0	10	10	4.59	173	96
72	30	0	0	500	500	4.58	172	100
73	1000	100	100	0	0	3.04	136	96
74	1000	100	0	100	0	3.05	136	97
75	1000	100	0	0	100	3.04	135	96
76	1000	0	100	100	0	3.06	137	97
77	1000	0	100	0	100	3.06	138	98
78	1000	0	0	100	100	3.07	138	99
79	5000	500	500	0	0	2.96	132	100
80	5000	500	0	500	0	2.96	132	100
81	5000	500	0	0	500	2.97	133	100
82	5000	0	500	500	0	2.98	134	100
83	5000	0	500	0	500	2.97	133	100
84	5000	0	0	500	500	2.97	133	100
85	8000	100	100	0	0	2.74	119	99
86	8000	500	500	0	0	2.75	120	100
87	8000	100	0	100	0	2.76	121	99
88	8000	500	0	500	0	2.75	120	100
89	8000	100	0	0	100	2.75	121	99
90	8000	500	0	0	500	2.76	121	100
91	8000	0	100	100	0	2.76	122	99
92	8000	0	500	500	0	2.77	122	100
93	8000	0	100	0	100	2.77	122	99
94	8000	0	500	0	500	2.78	123	100
95	8000	0	0	100	100	2.76	122	99
96	8000	0	0	500	500	2.77	123	100

[0017]

[Table 3]

No.	合金組成(ppm)		腐食減量 (mg/cm²)	ガス発生量 (ml)	圧延加工性 (%)
	Pb	Cd			
1	1600	400	4.68	181	100

[0018]

[Table 4]

No.	合金組成 (ppm)					腐食減量 (mg/cm²)	ガス発生量 (ml)	圧延加工性 (%)
	Bi	Mg	Ca	Sr	Ba			
2	10	0	0	0	0	4.51	165	48
3	30	0	0	0	0	4.52	166	51
4	30	5	0	0	0	4.54	168	63
5	30	0	5	0	0	4.55	169	63
6	30	0	0	5	0	4.54	168	62
7	30	0	0	0	5	4.55	169	62
8	30	2000	0	0	0	4.86	185	100
9	30	0	2000	0	0	4.89	188	100
10	30	0	0	2000	0	4.87	188	100
11	30	0	0	0	2000	4.90	189	100
12	8000	0	0	0	0	2.73	118	65
13	8000	5	0	0	0	2.76	121	71
14	8000	0	5	0	0	2.76	121	71
15	8000	0	0	5	0	2.77	122	70
16	8000	0	0	0	5	2.76	122	70
17	8000	2000	0	0	0	3.25	150	100
18	8000	0	2000	0	0	3.26	150	100
19	8000	0	0	2000	0	3.28	152	100
20	8000	0	0	0	2000	3.27	151	100
21	8000	1000	1000	0	0	3.28	151	100
22	8000	1000	0	1000	0	3.29	152	100
23	8000	1000	0	0	1000	3.26	150	100
24	8000	0	1000	1000	0	3.27	153	100
25	8000	0	1000	0	1000	3.27	151	100
26	8000	0	0	1000	1000	3.29	155	100
27	10000	0	0	0	0	2.85	110	73

[0019]It turns out that the corrosion of a zinc alloy is controlled remarkably, so that from these tables and bismuth concentration increases in the zinc alloy which does not contain cadmium and lead. If it is a range whose sum total loadings of magnesium, calcium, strontium, and barium are 10-1000 ppm, it turns out that strip-processing nature is satisfactory.

[0020]When blending bismuth at 30-8000 ppm and the above result blended alkaline-earth metals in 10-1000 ppm, it turned out that it becomes what corrosion resistance and strip-processing nature should satisfy in the zinc alloy which does not contain cadmium and lead.

[0021]

[Effect of the Invention]As explained above, according to this invention, the good zinc alloy for negative electrodes of corrosion resistance and strip-processing nature is obtained without blending cadmium and lead, and the manganese dry battery of low pollution can be provided.

[Translation done.]